

Forces in Surface Films. Part I.—*Theoretical Considerations.*

Part II.—*Experimental Observations and Calculations.*

Part III.—*The Charge on Colloids.*

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PART I.

In an earlier paper* on the adsorption of vapours, the author was led to make the assumption that the specific volume of the last portion of fluid adsorbed from the saturated vapour phase was the same as the specific volume of the liquid in equilibrium with the vapour. This led to a consideration of the nature of the surface film, and certain consequences of the variation in density there from the density of the liquid in bulk were immediately obvious, and are discussed below. Experimental proof of one of these was easily obtained by the author, and, recently, certain other observers, approaching the subject from a different aspect, have published evidence† with a promise of further work.

Let us consider the determination of the density of a finely divided solid by the usual immersion method, assuming that all gases such as air have been removed from the solid and the pure liquid. Let us assume that upon the surface of the solid there is a film amounting to α gm. liquid per gramme solid where the mean specific volume of the liquid is v_2 instead of v_1 , the value for the liquid in bulk. If the true specific volume of the solid is v , and v_0 is the volume ordinarily observed and calculated without regard to α , then, from a consideration of the total volume occupied by a gramme of the solid and the accompanying film, we see that

$$v + \alpha v_2 = v_0 + \alpha v_1$$

and \therefore

$$v = v_0 + \alpha (v_1 - v_2). \quad (1)$$

The second term on the right-hand side of (1) will only assume importance in the case of substances with a very large specific surface, and here, owing to the different compressibilities of various liquids, it seems reasonable to

* 'Trans. Faraday Soc.,' vol. 10, p. 167 (1914).

† Cude and Hulett, 'Jour. Amer. Chem. Soc.,' vol. 42, p. 391 (1920).

expect $\alpha(v_1 - v_2)$ to vary from liquid to liquid, and hence v_0 to vary from liquid to liquid. This, in fact, has been observed by the author and others.

There is a second source of variation of v_0 , for the surface may not be equally accessible to molecules of different liquids. Thus there may be a portion of the surface accessible to a water molecule (van der Waals' $b = 14 \times 10^{-4}$), but not accessible to a chloroform molecule ($b = 45 \times 10^{-4}$). We may therefore regard v as the space embraced by 1 gm. of the solid and not occupied by the liquid molecules when immersed in the liquid of greatest penetrating power, which for all practical purposes is water. We may conceive of a particle of the solid as possessing regions h, h, h , which are holes not accessible even to water molecules or ions, while another hole, k , is accessible to water but not to chloroform. Hence v includes the portions of space h, h, h , and, for water, equation (1) holds. On the other hand, if we denote the volume of the portions k by the symbol Δv , the equation for chloroform is

$$v + \Delta v' = v_0' + \alpha'(v_1' - v_2'), \quad (2)$$

where the dashes refer the various quantities to chloroform. Hence with a substance of surface not equally accessible to different liquids, we should be able to group determinations of the specific volume according to varying values of Δv , if we could determine the quantities on the right-hand side of (2). This grouping will presumably follow the order of molecular size.

Let us now assume we are dealing with a group of liquids for which the accessible surface of the solid under examination is the same. From equation (2), if we graph v_0 against $\alpha(v_1 - v_2)$ we will obtain a straight line whose intercept on the v_0 axis is $v + \Delta v$. But the value of $\alpha(v_1 - v_2)$ is not ordinarily known, for while α may be determined from observations on adsorption from the vapour phase and v_1 is known, v_2 remains undetermined save from theoretical considerations. If we could select a function of $\alpha(v_1 - v_2)$, we would obtain a curve giving the required intercept on plotting such a function against v_0 , but there is no obvious function available. On the other hand, it seems reasonable to assume that the less compressible a liquid is the smaller the value of $\alpha(v_1 - v_2)$. Thus for an incompressible liquid $v_1 = v_2$, and here, therefore, $v_0 = v + \Delta v$. Hence, if we could obtain observations on a sufficient number of liquids with different compressibilities, it should be possible to extrapolate to a value of $v + \Delta v$ from the (β, v_0) curve. Once this value was obtained equation (2) would give us $\alpha(v_1 - v_2)$ and if α and v_1 were known v_2 would be known, and hence also the compressive (or distensive) force

acting on the interfacial film. Denoting by p the pressure which changes v_1 to v_2 , and by β the mean compressibility of the liquid for the range of pressure considered we have

$$v_1 - v_2 = pv_1\beta$$

and \therefore

$$v + \Delta v = v_0 + \alpha pv_1\beta. \quad (3)$$

Since β varies somewhat with p , it is evidently desirable to have an estimate of the magnitude of p (which again may vary from liquid to liquid) before we can select the values of the compressibility to be used as indicated above, and so recourse must be made to theoretical considerations:

The author has previously* identified the compressive force in question with those giving rise to cohesion in liquids and represented by the term a/v^2 in van der Waals' equation,

$$(p + a/v^2)(v - b) = RT.$$

Since the attraction of a liquid for itself is represented approximately by the expression a/v^2 or $a^{\frac{1}{2}}/v \times a^{\frac{1}{2}}/v$ we may assume that the attraction between the solid and the liquid in the film is approximately represented by $a_0^{\frac{1}{2}}/v \times a^{\frac{1}{2}}/v_2$ where a_0 and v refer to the solid and a and v_2 to the liquid. This is the attraction per unit area across the interface solid-liquid. We may now conceive two cases to arise according as the adsorbed fluid is almost entirely surrounded by the adsorbent, that is, in capillary tubes or is only bounded on one side by the adsorbent. In the first case it is easy to conceive of the whole adsorbed fluid as being under the cohesive attraction of the adsorbent provided the capillaries are sufficiently small. In the second case the compression will be very great in the molecular layer next the adsorbent and fall rapidly to zero within a few layers. We may, therefore, for purposes of calculation assume the interfacial film in this case to be in two parts, one half being highly compressed under the influence of the adsorbent while the compression in the other half under attraction of the liquid is relatively small. In the first case we assume that the total amount adsorbed α is compressed, in the second case that only $\frac{1}{2}\alpha$ is compressed. It is obvious that these assumptions could be made with regard to the calculations based on the graphical method suggested in the preceding paragraph, and in any case the first assumption will lead to a smaller estimate of the mean compressive force acting on the adsorbate, since a greater volume is compressed. This assumption we will adopt, taking the whole fluid in the adsorption layer as of specific volume v_2 , under an attractive force $a_0^{\frac{1}{2}}/v \times a^{\frac{1}{2}}/v_2$. This force will function, both as an external pressure

* 'Roy. Soc. Proc.,' vol. 96, A, p. 287 (1919).

and as an "internal" pressure so that the fluid in the film will be as if under an external force p such that

$$p + a/v_2^2 = a_0^{3/2}/v \times a^{3/2}/v_2. \quad (4)$$

Equation (4) may also be derived by considering that the pull inwards of the adsorbent will be opposed by the internal cohesion of the film itself leaving an excess p to function as a pressure. From (4) we derive an expression for p as

$$p = a^{3/2}/v_2 (a_0^{3/2}/v - a^{3/2}/v_2), \quad (5)$$

and an expression for $a_0^{3/2}/v$ as

$$a_0^{3/2}/v = (p + a/v_2^2)/a^{3/2}/v_2. \quad (6)$$

Since observations on the compression of a liquid give us the relation between p and v_2 , if we determine one of these we can further determine a_0/v^2 or the "internal" pressure of the adsorbent.

PART II.

Determination of v_0 .

The substance selected as possessing a surface large enough to give the effect sought for was blood charcoal. Some highly purified material was dried in an oven at 120° C. and subsequently transferred to a desiccator over phosphorus pentoxide where it was kept several weeks. The specific volume was determined by the usual method employed in the case of powders using a silica specific gravity bottle of approximately 50 c.c. Two liquids were employed, water and chloroform. About 2 grms. of the charcoal were rapidly weighed in the specific gravity bottle and then covered with the liquid. The bottle was now placed in a bath of the liquid and the temperature raised to the boiling point with careful stirring, and kept there for several hours. The bottle was then completely filled with the freshly boiled liquid and the stopper inserted at a marked position. The stopper had a cup-shaped top in which was placed excess of the liquid to allow for contraction and evaporation during immersion in the thermostat. After sufficient immersion the meniscus was adjusted, the cup stoppered, and the bottle removed, cooled to weighing-room temperature, dried, and subsequently weighed. It was found possible by this simple method* to obtain readings with chloroform alone at 25° C., whose variation from the mean was not more than 1 mgrm., corresponding to an error of 0.01° in the thermostat temperature. In the subsequent calculations the weight of the charcoal was corrected for the

* Those experiments were made in 1919 before the publication of the paper by Cude and Hulett. They were first attempted in 1916 with a glass s.g. bottle.

adsorbed gases which were present when it was weighed, and which were expelled on immersion in the liquid. The values of v_0 thus obtained were consistent within 0.2 per cent. A specimen determination and calculation is given below in Table I, where *ic* is the correction for adsorbed gases, and

Table I.

Duration of boiling.....	3 hours.	6 hours.	10 hours.	13 hours.
Temperature of thermostat	25°·02 C.	24°·88 C.	24°·95 C.	24°·94 C.
Mass in air of CHCl ₃	74·097	74·111	74·104	74·105
" " charcoal	1·877	1·877	1·877	1·877
" " CHCl ₃ and charcoal	75·974	75·988	75·981	75·982
ΔCHCl ₃ + <i>ic</i>	74·660	74·677	74·675	74·672
<i>ic</i>	1·314	1·311	1·306	1·310
<i>c</i>	0·085	0·085	0·085	0·085
ΔCHCl ₃	1·792	1·792	1·792	1·792
Volume of CHCl ₃	1·229	1·226	1·221	1·225
Spec. vol. of charcoal	0·830	0·828	0·825	0·827
	0·463	0·462	0·460	0·462

ΔCHCl₃ the mass in air of the chloroform apparently displaced by the evacuated charcoal, *c*. It will be seen that after several hours' boiling, consistent results were obtained. The chloroform was the purest B.P. chloroform, which was found free from charring on shaking with concentrated sulphuric acid. It was shaken up with water to dissolve out alcohol and then treated with fused calcium chloride, to remove water, and subsequently with fused caustic potash, to destroy carbonyl chloride, etc., decanted, and distilled. On fractional distillation practically the whole preparation passed over between 61.4°–61.5° at 76.4 cm. pressure. Three determinations of the chloroform in the s.g. bottle (50.095 c.c.) at 25° C. gave 74.149, 74.149, and 74.147 grm., corrected to vacuo. The mean value gave a density of 1.48016 grm. per cubic centimetre at 25° C., while a second preparation gave 1.48007. After decantation from the charcoal the density of the first preparation was found to be 1.48010 (one determination). The divergence is within the limits of errors of observation and there is no evidence of anything being imparted to, or withdrawn from, the chloroform upon contact with the adsorbent. It may be mentioned that the density at 25°, as determined by Thorpe was 1.4791, while Pierre gives 1.4803.

The values of v_0 for water were found to be 0.510 and 0.512 at 25° C., and 0.518 and 0.519 at 40° C., while for chloroform the values were 0.460 and 0.461 at 25° C. Thus at 25° C. the mean values were 0.511 and 0.461, a

divergence well outside any possible experimental error. It may here be pointed out that any error in the correction for gases adsorbed and subsequently expelled would alter the values in practically the same proportion.

We may compare these results with those obtained by Cude and Hulett (*loc. cit.*) from their less finely divided charcoal. This is done in Tables III and IV. Here the last column gives the compression at 20° C. of the given

Table III (Williams).

Liquid.	v_0 .	b .	$p\beta$.
H ₂ O	0·511	14×10^{-4}	0·020
CHCl ₃	0·461	45	0·036

Table IV (Cude and Hulett).

Liquid.	v_0 .	b .	$p\beta$.
H ₂ O	0·539	14×10^{-4}	0·020
CS ₂	0·504	34	0·036
C ₆ H ₆	0·556	54	0·034
CCl ₄	0·607	57	0·038

liquid under a pressure of 500 atmospheres. The data are taken from Bridgman* and from Richards.† It will be seen that in the case of Table III the compressibility appears to be a chief factor determinating the value of v_0 , while in Table IV the determinations fall into two groups according as b is greater or less than, say, 40×10^{-4} , that is, while we may assume that the charcoal used by the present author had a surface equally accessible to water and chloroform molecules, this assumption could scarcely be made for the other specimen and liquids employed. This is in accordance with the theory developed in Part I. It may also be pointed out that benzene‡ freezes at 25° C. under a pressure of about 670 atmospheres with a change in volume of 0·11 c.c. per gramme while carbon tetrachloride at 25° C. freezes under about 1,400 atmospheres with a change in volume of only 0·02 c.c. per gramme. This may not be unconnected with the variation of v_0 observed, which is certainly in the required direction, the compression of the benzene under suitable pressure being greater than that of the carbon tetrachloride.

It is obvious that if the surface of the first charcoal was not so accessible to

* 'Proc. Amer. Acad. Arts and Sc.,' vol. 47, p. 411 (1912); vol. 49, p. 1 (1913).

† Richards, Stull, Mathews, and Speyers, 'Jour. Amer. Chem. Soc.,' vol. 34, p. 988 (1912).

‡ Bridgman, 'Phys. Rev.' (2), vol. 3, pp. 126, 153 (1914).

the chloroform as to the water, an increase in the accessibility to the chloroform would *reduce* the corresponding v_0 value both because more space would be occupied by the chloroform and because the extra chloroform would be compressed. (We are not considering such a splitting up as would sensibly reduce the cohesive forces of the adsorbent.) A correction thus introduced would lower the value of the right-hand side of (7) below and reduce to some extent the estimate of the cohesive forces.

Determination of α and Calculation of the Surface Cohesion.

Several years ago* the author made a series of observations on the mass of vapour picked up at 25° C. by 1 gram. of evacuated charcoal from the saturated vapour of different liquids. He was unable to detect any regularity in the results, such as, for example, that of equal volumes found by Bachmann† with silica and by Gurvich‡ with fuller's earth which led these authors and Langmuir§ to conclude that the approximately equal volumes represented the volume of capillary pores of the adsorbent. Because of the lack of any simple relation among the values found, the experiments were never published, but the determinations on water and chloroform have now proved useful. The charcoal was evacuated at 100° C. by a Töpler pump, *i.e.*, under conditions comparable with the boiling out underneath the liquid in the later experiments. After making all corrections, the mean of two closely concordant observations at 25° C. gave for water 0.75 gram. and for chloroform 1.26 gram. Hence the volume of the water adsorbed was 0.75 c.c. and of the chloroform 0.85 c.c. These volumes are not equal, nor apparently are the volumes under compression on the adsorbent, for then we would have

$$v_0 + \alpha v_1 = v_0' + \alpha' v_1',$$

which is not true. Instead we have the equations

$$\begin{aligned} v &= 0.511 + 0.75(1 - v_2/v_1), \\ &= 0.461 + 0.85(1 - v_2'/v_1'), \end{aligned}$$

whence

$$0.85 v_2'/v_1' - 0.75 v_2/v_1 = 0.5. \quad (7)$$

Knowing the variation in volume of water and chloroform under pressure, we can tabulate pressures which fulfil condition (7). The variation in volume is presented in Table V, where it has been assumed that the film of

* Liverpool, 1912-13. The author wishes to acknowledge here his indebtedness to Prof. F. G. Donnan, F.R.S., for his encouragement and advice in the execution of these apparently profitless experiments.

† 'Z. f. Anorg. Chem.,' vol. 79, p. 202 (1912).

‡ 'J. Russ. Phys. Chem. Soc.,' vol. 47, p. 805 (1915).

§ 'J. Amer. Chem. Soc.,' vol. 39, p. 1848 (1917).

Table V.

Pressure.	Relative volume.			
Hgrm./Cm. ²	Water.		Chloroform.	
1	1.00	0.75	1.00	0.85
1,000	0.96	0.72	0.93	0.79
3,000	0.91	0.68	0.86	0.73
5,000	0.87	0.65	0.82	0.70
7,000	0.84	0.63	0.79	0.67
9,000	0.81	0.61	0.77	0.65
11,000	0.80	0.60	0.75	0.64

chloroform did not freeze, and that its compressibility was closely the same as that of isobutyl alcohol.* In Table VI are then given the pressures satisfying equation (7). Corresponding to these pressures, we may evaluate $a_0^{\frac{1}{2}}/v$ by means of equation (6), and find when the two values from the two liquids coincide. This evaluation is given in Table VII, where the values of "a" for chloroform and for water have been taken as 2930×10^{-5} and 1089×10^{-5} respectively, leading to cohesions at atmospheric pressure and 25° C. of 2300 kgrm./cm.² and 17,300 kgrm./cm.²

Table VI.

CHCl ₃ .		H ₂ O.	
p.	$p + a/v_2^2$.	p.	$p + a/v_2^2$.
1,000	3,700	300	18,000
7,000	10,700	8,000	33,000
9,000	12,900	10,000	37,000
10,000	13,900	11,000	38,000
11,000	15,000	12,000	40,000

Table VII.

$a_0^{\frac{1}{2}}/v$.	
CHCl ₃ .	H ₂ O.
0.7×10^2	1.3×10^2
1.8	2.1
2.1	2.2
2.2	2.3
2.4	2.4

From Table VII, we see that the required coincidence in the $a_0^{\frac{1}{2}}/v$ values only occurs when the chloroform and water are under pressures of 11,000 kgrm. and 12,000 kgrm. per cm.² respectively.

Now, chloroform in bulk freezes at 25° C. under 5500 kgrm. pressure and water at 9800 kgrm. (Bridgman). If solidification takes place in the adsorption layer, the effect would be a diminution of the volume of the chloroform of 0.045 c.c. per gramme, which would push the corresponding pressure for

* In a private communication to the author, P. W. Bridgman states that the compressibility at 40° was practically the same as that of isobutyl alcohol. The author desires to acknowledge his indebtedness for this information.

water above 10,000 kgrm., that is, the order of magnitude of the compressive forces is not affected.* Keeping, however, to our assumption of a liquid film, we see that the compression in the chloroform is from 0.85 c.c. to 0.64 c.c., or 0.21 c.c. in all, whence the specific volume of the charcoal is not 0.46 but $0.46 + 0.21$, or 0.67 c.c. The water observation naturally leads to the same result.

We also have at our disposal an estimate of the internal cohesion of the charcoal. To satisfy equation (7) and equation (6) for the two liquids, a_0^3/v had to be 2.4×10^2 , whence a_0/v^2 is 58,000 kgrm. per cm.², an internal pressure three times that of water at ordinary temperatures and pressures.

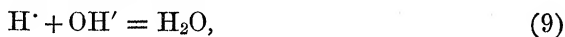
PART III.

Having obtained an estimate of the compressive force in an adsorption layer it is of interest to examine some consequences of the existence of a force of this magnitude. Lagergren†, assuming the force to be of the order of 10,000 atmospheres—curiously enough the same estimate as that found in Part II above—calculated the effect on the solubility of different salts in aqueous solution and correlated it with the positive or negative adsorption he found for them with kaolin and charcoal. We will, however, confine our attention to the case of a finely divided substance in suspension in pure water, and examine the effect on the dissociation of the water (assumed liquid) in the adsorption layer.

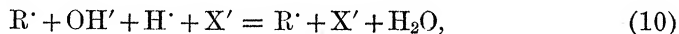
The effect of pressure on a chemical reaction in solution has been investigated thermodynamically by Planck‡ who deduced the relation.

$$\frac{d \log K}{dP} = \frac{V_1 - V_2}{RT}, \quad (8)$$

where K is the equilibrium constant, P the pressure and $V_1 - V_2$, the volume change during the reaction. The reaction here considered is:—



where the total volume change may be estimated from the volume change in a reaction of the type



* Such solidification, if it exists, could be detected by dilatometric measurements which would thus furnish an independent estimate of the pressure from the temperature determination. We are not dealing with liquid in wide capillaries such as is found in some silica gels and lamp black, upon which observations of this nature have been made. See Foote and Saxton, 'Journ. Amer. Chem. Soc.,' vol. 39, p. 627, etc. (1917).

† 'Bihang till K. Svenska Vet. Akad. Handl.,' vol. 24, II, p. 4 (1898).

‡ 'Thermodynamics,' 1903, equation (220). See also Williams, 'Trans. Faraday Soc.' (in the press).

that is, the neutralization of a strong base by a strong acid in dilute solution. Ostwald* found the neutralisation of normal solutions of strong acids by strong bases led to an increase in volume of approximately 20 cc. By far the greater part of this increase is due to the reaction in equation (9). By extrapolating to infinite dilution for the molar volumes of a few acids, bases, and salts given in Landolt-Börnstein the author found that the change of volume involved lay between 18 and 22 cc., in agreement with Ostwald's direct determination. We may therefore take 20 cc. as the value of $V_1 - V_2$ in equation (9) and calculate the value of the right-hand side. We have

$$\frac{d \log K}{dP} = \frac{V_1 - V_2}{RT} = \frac{20 \times 273}{22400 \times 298}$$

or
$$\frac{d \log_{10} K}{dP} = \frac{20 \times 273}{2.3 \times 22400 \times 298} = 0.0036,$$

when P is expressed in atmospheres. Integrating on the assumption that $V_1 - V_2$ is appreciably constant we have approximately

$$\log_{10} K_2 - \log_{10} K_1 = 0.0036 (P_2 - P_1)$$

so that when P_2 is 12,000 atmospheres we have

$$\log_{10} K_{12000} = \log_{10} K_1 + 4.3 = 14.0 + 4.3 = 18.3,$$

whence the concentration of H^+ and OH' is 10^{-5} in the adsorption layer as against 10^{-7} in the water outside.

We may expect as a result of this increased concentration of ions in the adsorption layer that a diffusion potential will be set up of the same type as has been investigated by Nernst, who gives for the diffusion potential difference between two solutions of ionic concentrations c_1 and c_2 respectively the well-known formula

$$E = \frac{RT}{n} \frac{u-v}{u+v} \log c_1/c_2.$$

Assuming that u and v are equally affected by the compression this formula becomes at 25° C. for H^+ and OH' .

$$\begin{aligned} E &= 0.016 \times \log_{10} c_1/c_2 = -0.016 \times \frac{1}{2} \log_{10} K_{12000}/K_1 \\ &= -0.16 \times \frac{1}{2} \times 4.3 = -0.034 \text{ volts,} \end{aligned}$$

that is, the adsorption layer will have a potential 0.034 volts lower than the surrounding fluid, and the charcoal particle will thus appear to be negatively charged when immersed in pure water. The order of magnitude of this calculated potential difference agrees with observations made on particles suspended in water. Since graphite appears negatively charged,† a negative

* 'J. Prakt. Ch.' (2), vol. 18, p. 353 (1878).

† Burton, 'Physical Properties of Colloidal Solutions,' p. 125.

sign is to be expected for charcoal particles. We, therefore, see that the existence in the adsorption layer of compressive forces of the magnitude given is sufficient to explain in sign and magnitude the potential differences and apparent charge on certain particles suspended in fluids.

From the simple theory outlined above we should expect that substances with a cohesion larger than water would appear negatively charged when immersed in it, while those with a smaller cohesion would appear positively charged. The positive ion of water moves faster than the negative ion, and we should have the reverse order of apparent change in a fluid giving rise to ions where the negative ion moves faster than the positive ion.

Confining our attention again to pure water, we see that, in order to give rise to an apparent positive change, the adsorption film must be not compressed, but distended. Even allowing an extremely small internal cohesion for any substance in suspension, it seems improbable that the magnitude of the distensive forces can be as great as those of the cohesive forces, and hence we would expect any observed positive potential differences to be less in magnitude than negative P.Ds. (ignoring "dilution" of the water). This is, however, not the case* and we therefore must look for some further source of P.D. Again, chloroform and various oil emulsions† have been reported as possessing negative changes, although the internal cohesions of chloroform and some oils are certainly less than the internal pressure of water. Since the concentrations of hydrogen and hydroxyl ions necessary to give rise to the observed P.D. are extremely small, very small concentrations indeed of an electrolyte would superimpose other electrical diffusion effects and so alter the magnitude and even the sign of the P.D. arising from the cohesive forces in the adsorption layer. Thus in the case of chloroform mentioned above any reaction in the adsorption layer giving rise to hydrochloric acid even to a very small extent would cause the chloroform particles to appear *negatively* charged, as is found, through the increased concentration of the hydrogen ions. In the same way instead of attributing a very small cohesion to ferric hydroxide sol, we might expect it to give rise to hydroxyl ions as well as some relatively immobile positive ions so that it appears positively charged.‡

We have now briefly discussed the theory that the origin of the apparent charge in colloids and suspensions lies in a diffusion potential difference arising from ions produced either by the action of cohesive forces on the adsorption layer or from ionisation direct or indirect of the dispersoid. It

* Burton, *loc. cit.*, p. 135.

† Burton, *loc. cit.*, p. 126.

‡ Compare also Duclaux, 'Jour. Chim. Phys.', vol. 5, p. 29 (1907).

seems of interest to examine very briefly the effect of the presence of electrolytes in the dispersion medium.

In the theory outlined above the sign of the P.D. is attributed to the tendency to diffusion away from the adsorption layer of excess of either fast moving hydrogen or hydroxyl ions. Thus with a negative colloid there is a greater concentration of H^+ in the adsorption layer than in the rest of the dispersion medium. Now, as is well known, Linder and Picton* found on precipitating arsenious sulphide, a negative colloid, with barium chloride, that the supernatant liquid was acid. It is obvious that preferential adsorption of the basic portion of the products of hydrolysis of a normal salt would leave outside the adsorption layer sufficient hydrogen ions to neutralise the effect of the hydrogen ions in the adsorption layer and so reduce or destroy the original potential difference with consequent precipitation of the colloid.

Summary of Parts I, II and III.

(1) Attention is directed to the effects of (i) accessibility of surface, and (ii) adsorption, on the apparent specific volume of finely divided solids.

(2) Observations are in agreement with the simple theory of these effects.

(3) The true specific volume of a specimen of charcoal which appeared to be 0.51 in water and 0.46 in chloroform, was evaluated as 0.67 c.c. per gramme.

(4) The attractive pressure in the surface film on the charcoal was calculated to be of the order of 10,000 atmospheres, while the internal pressure of the charcoal itself was estimated as of the order of 50,000 atmospheres.

(5) It is shown that such compressive forces may give rise in the adsorption layer to a diffusion potential difference of the magnitude observed in the case of suspensoids.

* 'Jour. Chem. Soc.,' vol. 67, p. 63 (1895), and vol. 87, p. 1906 (1905). See also Whitney and Ober, 'Jour. Amer. Chem. Soc.,' vol. 23, p. 842 (1901).